Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Harnessing Uranyl Oxo Atoms via Halogen Bonding Interactions in Molecular Uranyl Materials Featuring 2,5-Diiodobenzoic acid and N-Donor Capping Ligands

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I. Additional Single Crystal XRD Data

Table S1 Crystallographic data for the UO_2-3,5-dibromobenzoic acid-BPY complex **6**.

	6
chem formula	$C_{24}H_{14}N_2Br_4O_6U$
formula weight	984.04
cryst system	triclinic
space group	P-1
a (Å)	10.0684(18)
b (Å)	11.644(2)
c (Å)	12.261(2)
α (deg)	91.165(3)
β (deg)	113.983(2)
γ (deg)	90.210(3)
V (Å^3)	1312.9(3)
Z	2
T (K)	110(2)
λ (Mo Kα)	0.71073
D_{calc} (g cm^{-3})	2.489
μ (mm^{-1})	12.311
R_{int}	0.0426
R1 [$I>2\sigma(I)$]	0.0374
wR2 [$I>2\sigma(I)$]	0.0744

Complex **6** was not synthesized as part of our previous study[1] and thus was prepared and characterized as part of this work. Its inclusion allows for a more comprehensive comparison of structural and supramolecular systematics across these three families of complexes featuring dichloro-, dibromo-, and diiodobenzoic acid ligands and additional figures highlighting local structure and packing can be found below in Figure S1. The CIF for this material was deposited in Cambridge Structural Database and may be obtained from http://www.ccdc.cam.ac.uk by citing reference number 1501016.

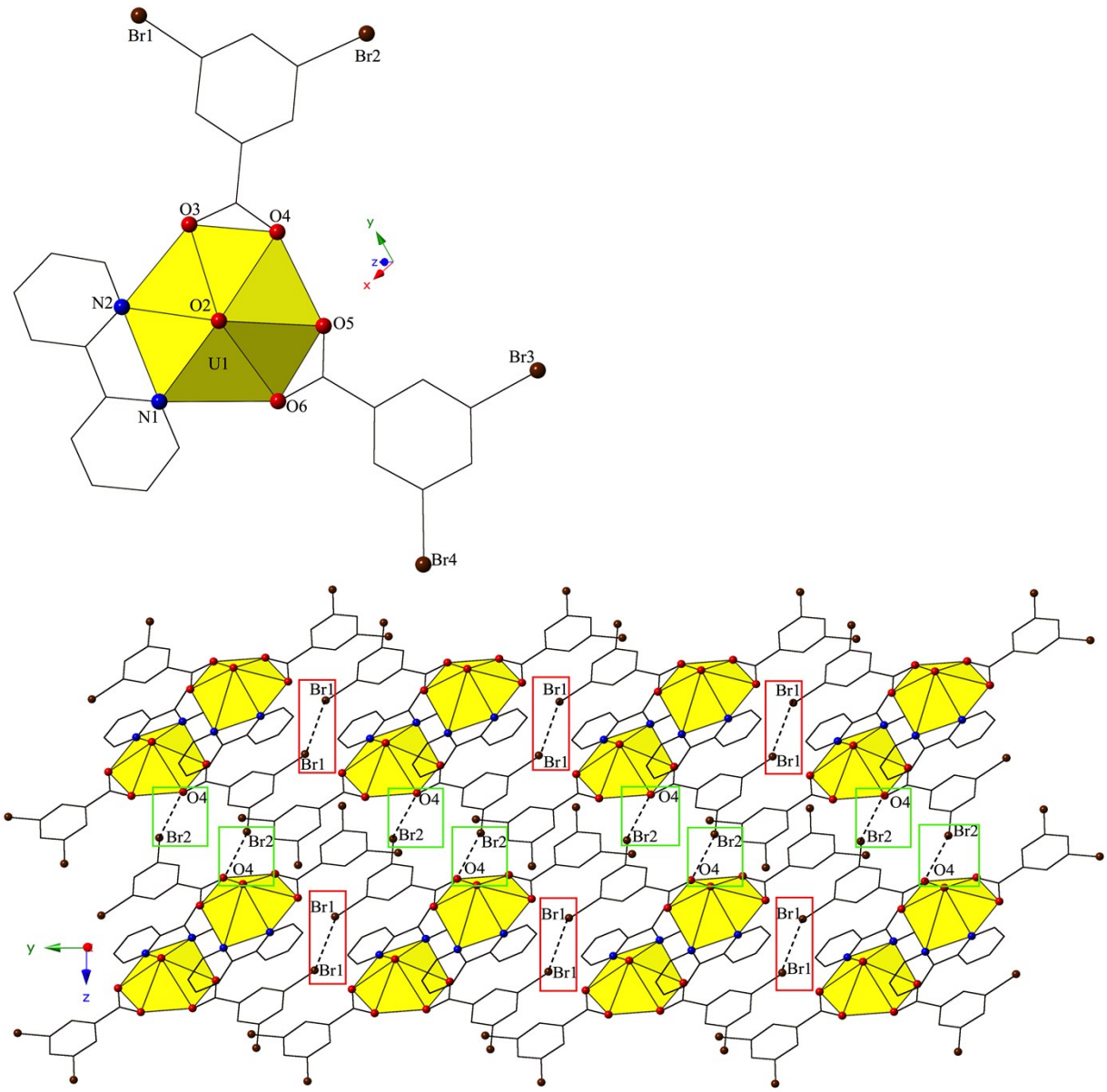

Figure S1 (Top) Polyhedral representation of local coordination geometry of **6**. Yellow polyhedra represent uranium metal centers, whereas brown, red, and blue spheres represent bromine, oxygen, and nitrogen atoms, respectively. All H atoms have been omitted for clarity. **(Bottom)** Complex **6** viewed in the (011) plane showcasing the halogen-halogen and halogen bonding interactions that assemble the monomers of **6** into a supramolecular 2D sheet.

II. Additional Figures

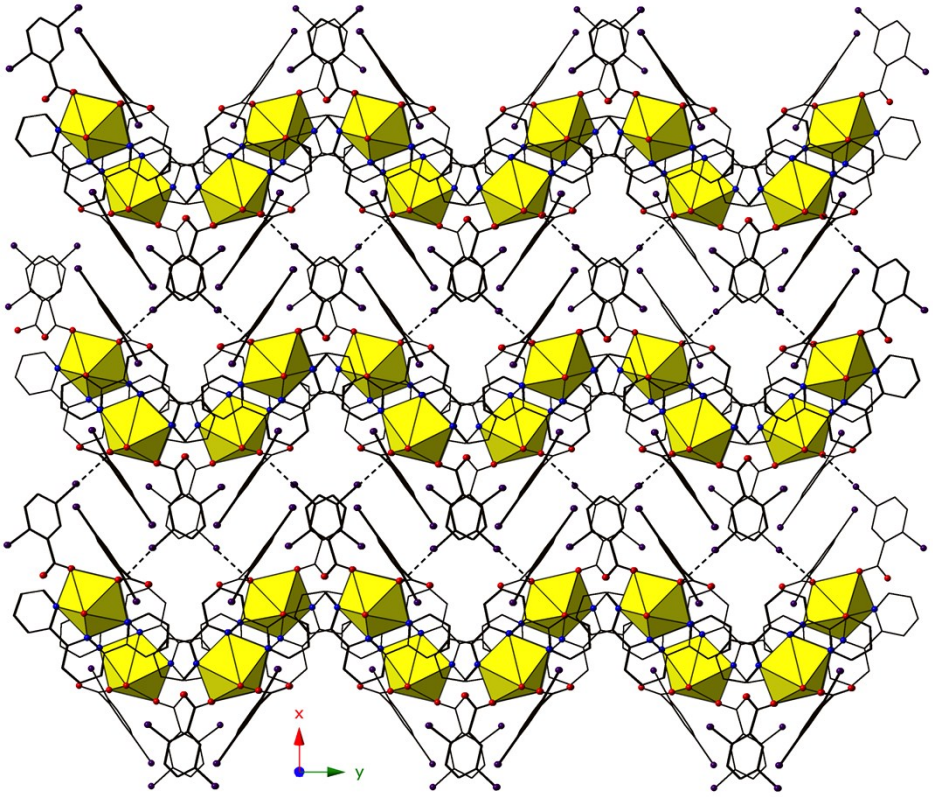

Figure S2 The undulating supramolecular 2D sheets of **4** viewed in the (110) plane. Halogen bonding interactions that tether 2D sheets into a 3D network are shown.

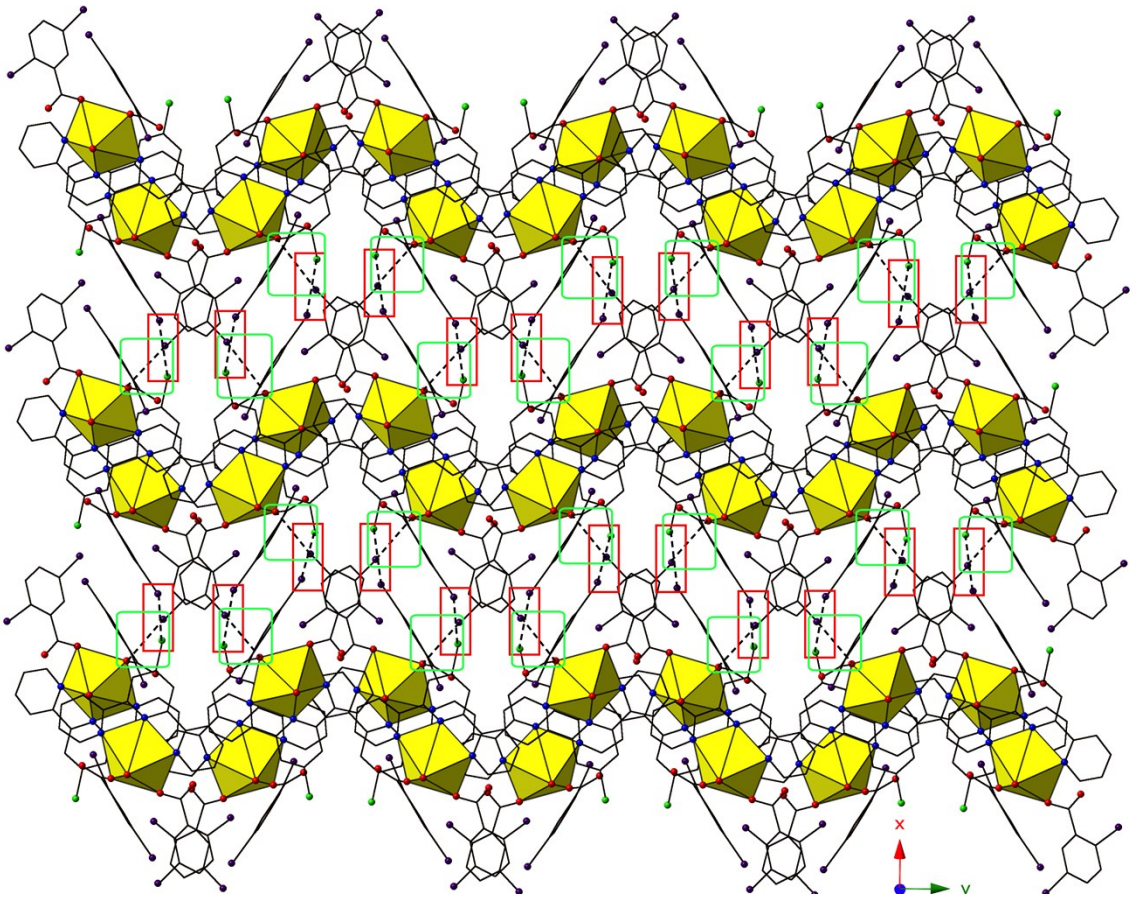

Figure S3 The undulating supramolecular 2D sheets of **5** viewed in the (110) plane. Halogen bonding interactions (green boxes) and Type I Cl-I interactions (red boxes) that assemble 2D sheets into a 3D network are highlighted.

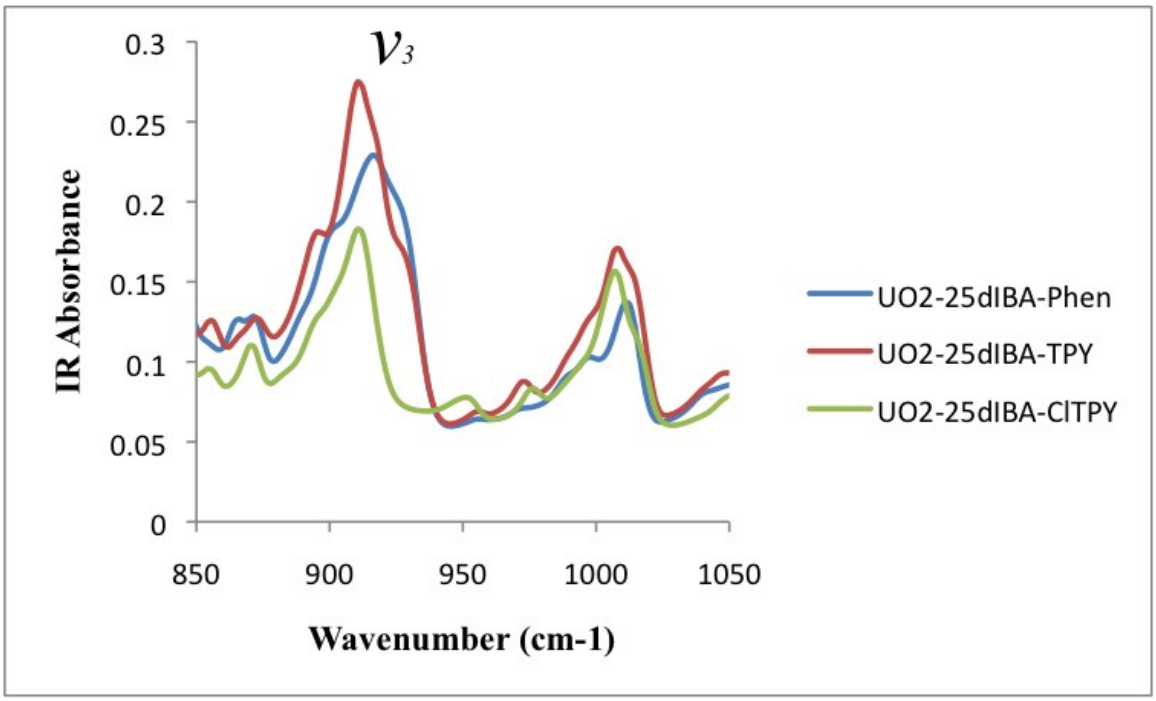

Figure S4 Infrared spectra of complexes **2** (blue), **4** (red), and **5** (green) highlighting the asymmetric stretch ν_3 of the uranyl cation in each material.

III. Powder X-ray diffraction data

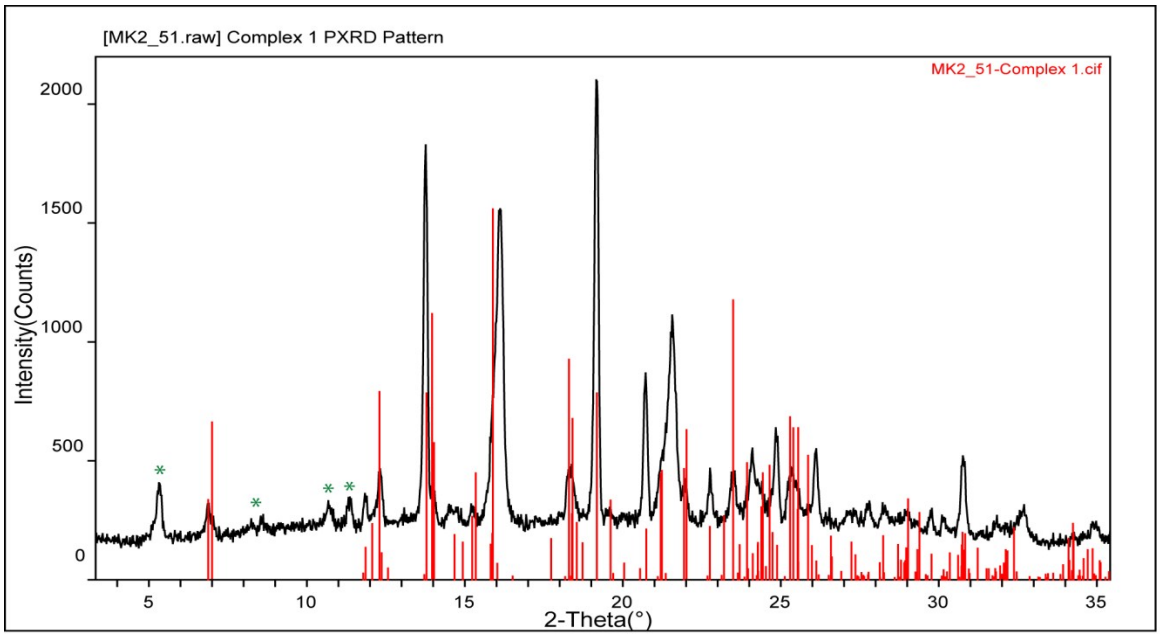

Figure S5 The observed PXRD pattern of structure **1** with calculated pattern overlaid in red. We acknowledge an impurity phase (or phases) as indicated with green asterisks.

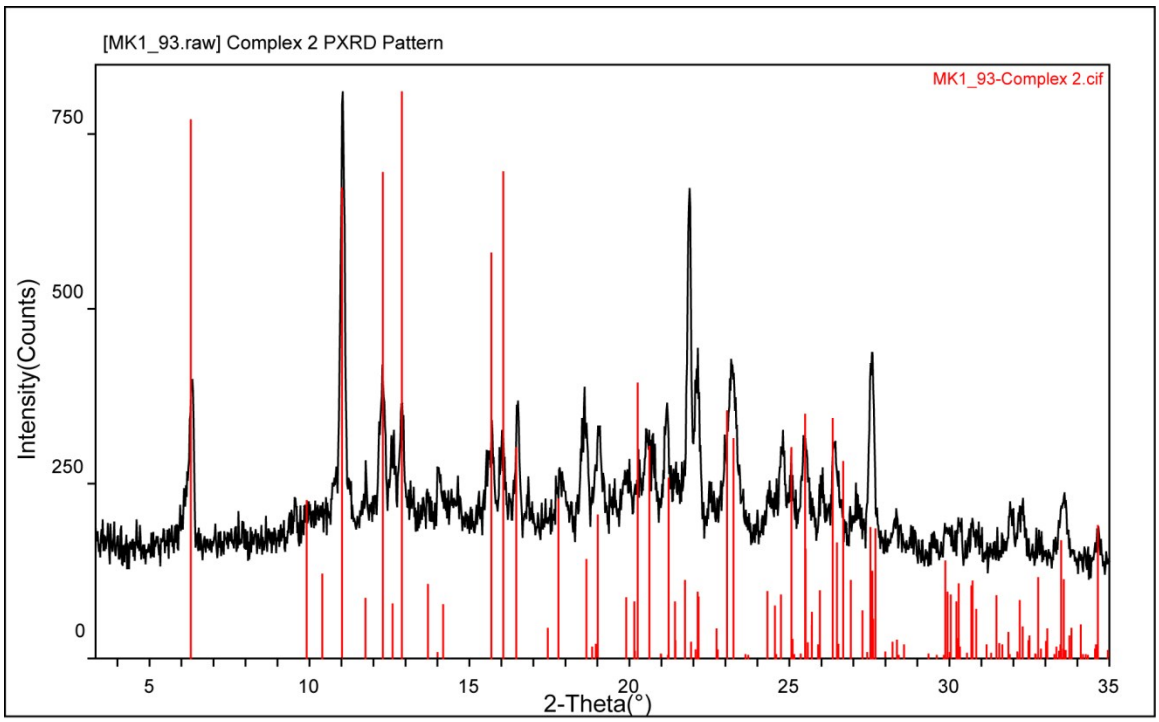

Figure S6 The observed PXRD pattern of structure **2** with calculated pattern overlaid in red.

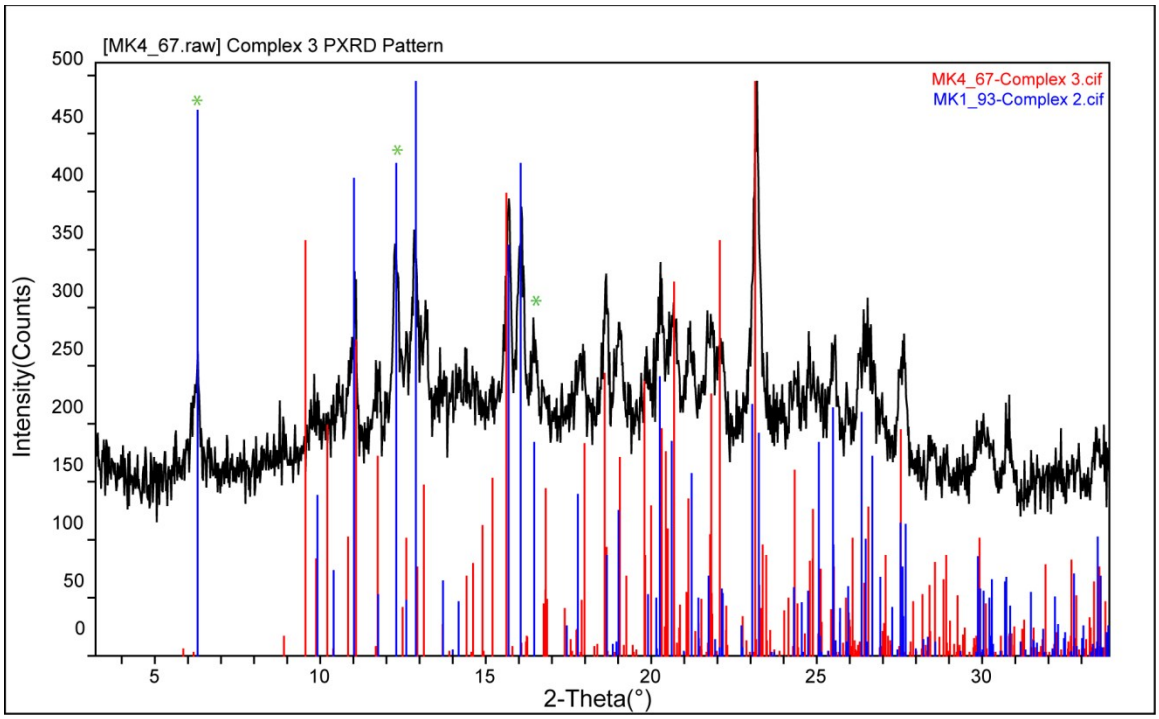

Figure S7 The observed PXRD pattern of structure **3** with calculated pattern overlaid in red. Impurities in **3** have been identified as complex **2** (calculated pattern overlaid in blue).

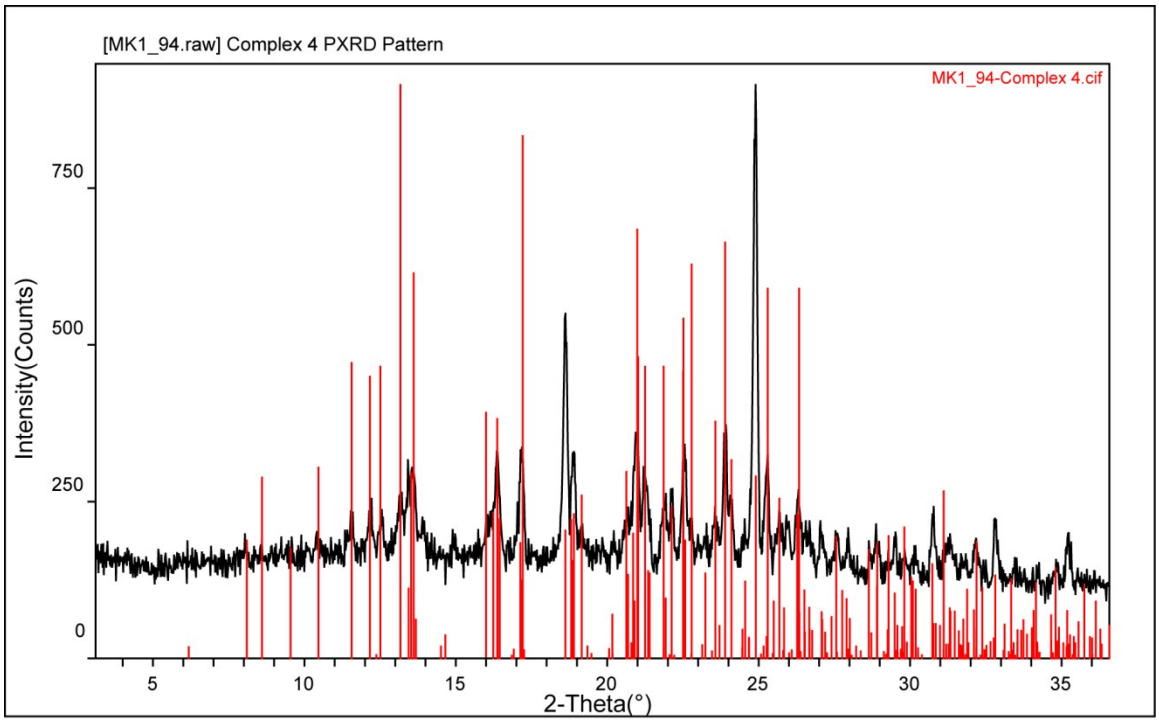

Figure S8 The observed PXRD pattern of structure **4** with calculated pattern overlaid in red.

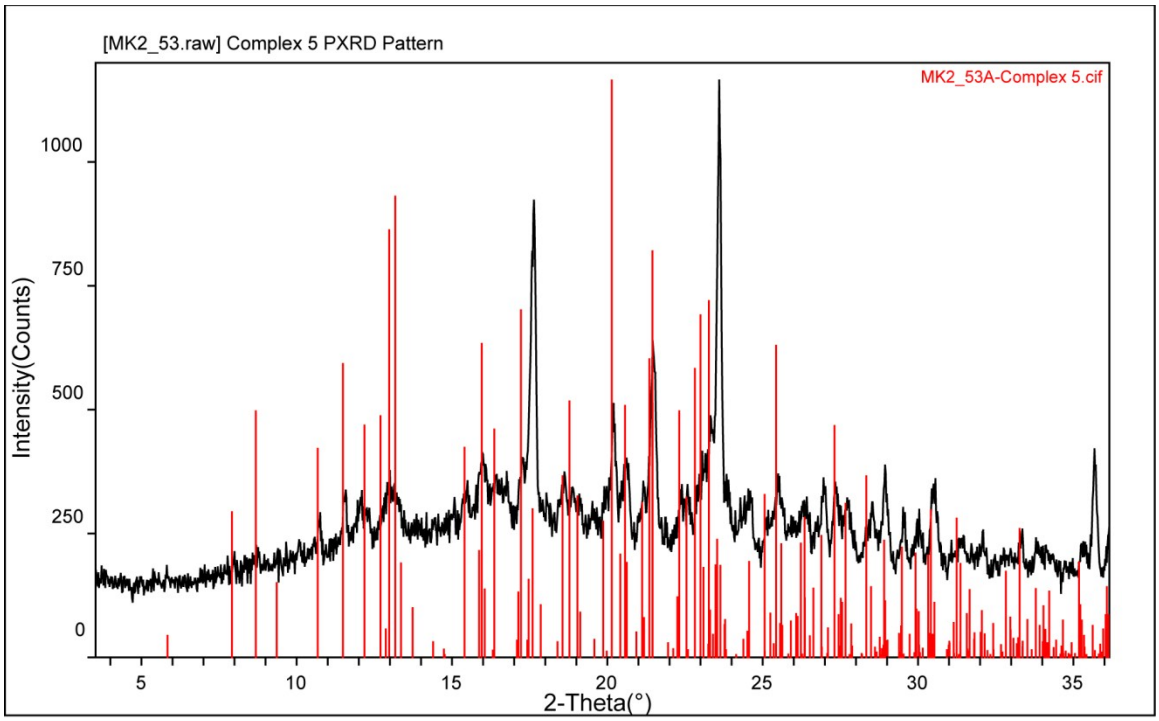

Figure S9 The observed PXRD pattern of structure **5** with calculated pattern overlaid in red.

IV. Thermal Ellipsoid Plots

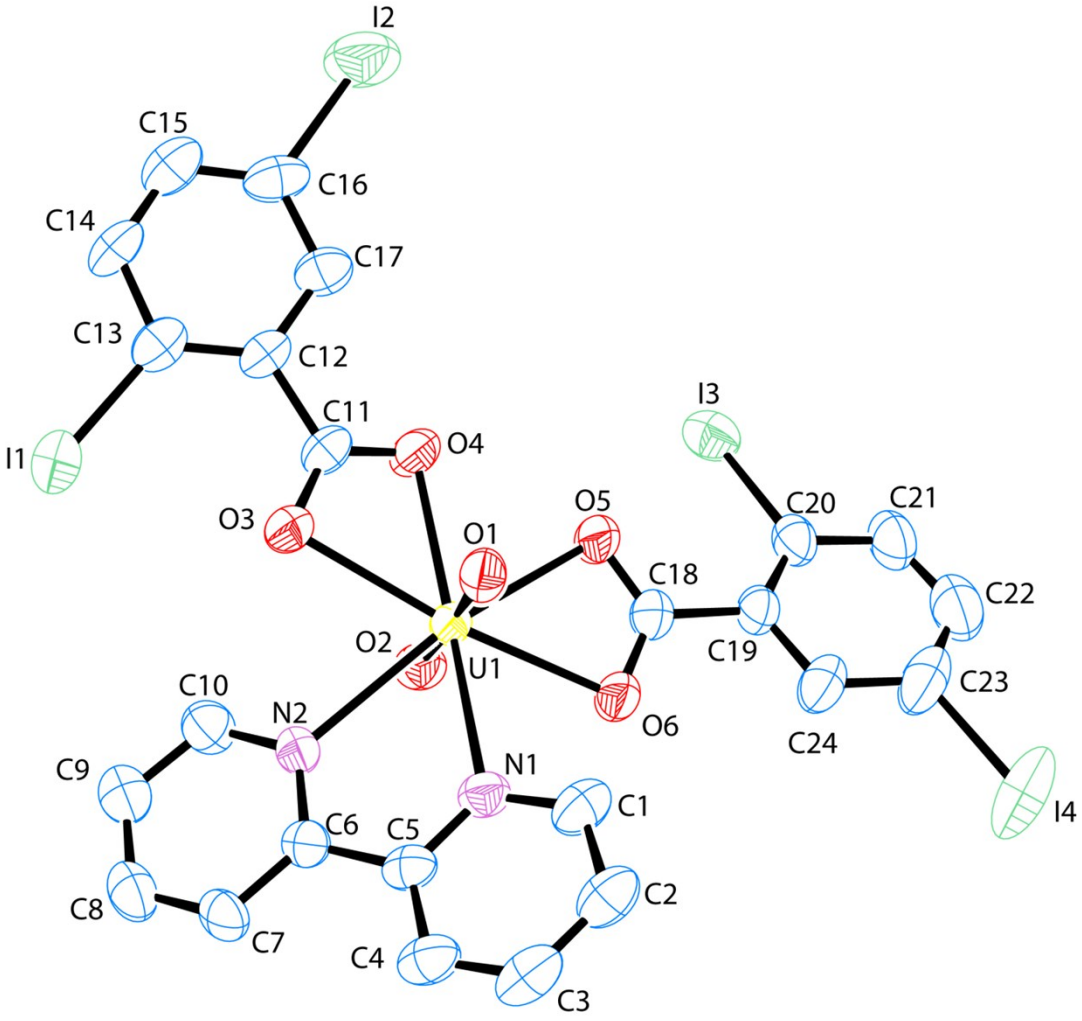

Figure S10 ORTEP illustration of complex **1**. Ellipsoids are shown at 50% probability level.

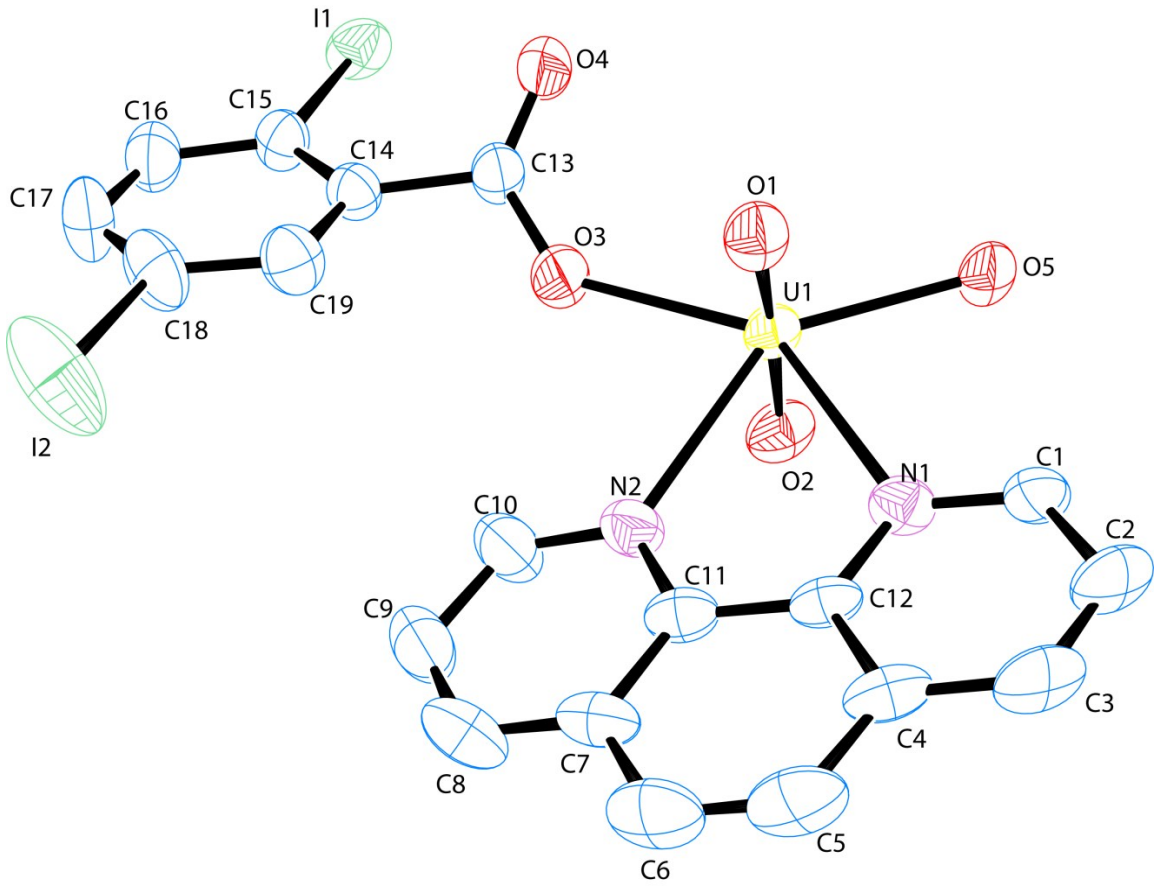

Figure S11 ORTEP illustration of complex **2**. Ellipsoids are shown at 50% probability level.

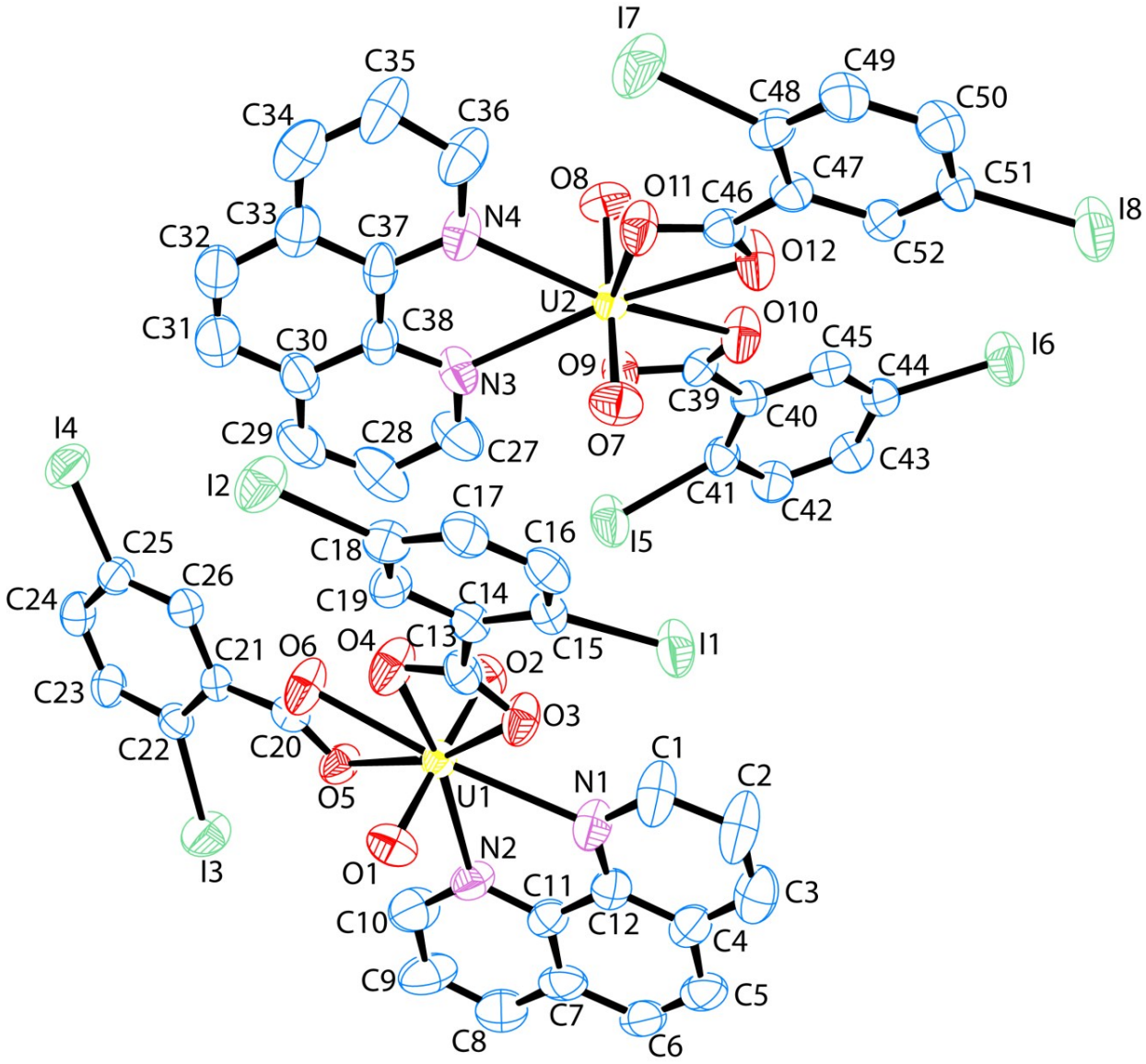

Figure S12 ORTEP illustration of complex **3**. Ellipsoids are shown at 50% probability level.

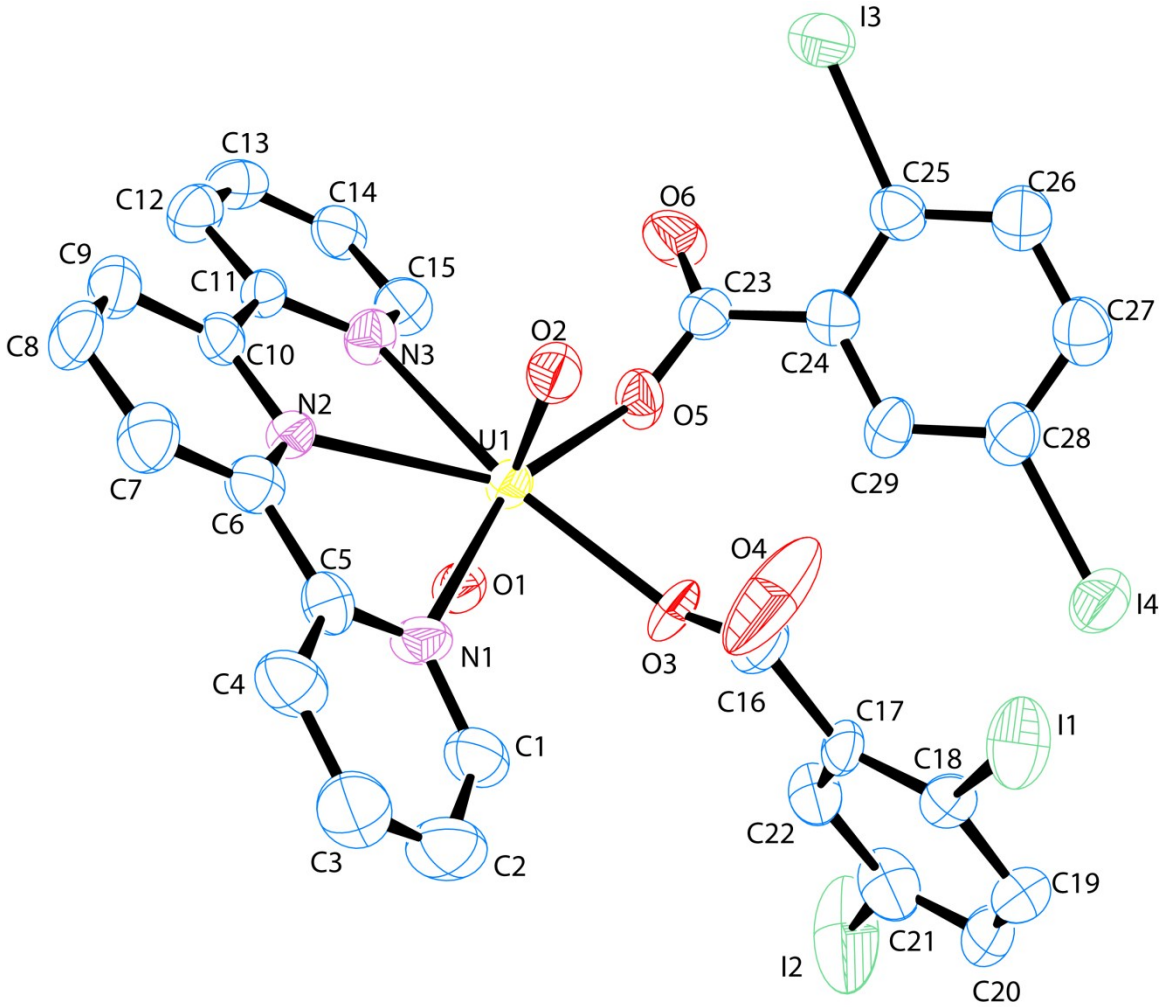

Figure S13 ORTEP illustration of complex **4**. Ellipsoids are shown at 50% probability level.

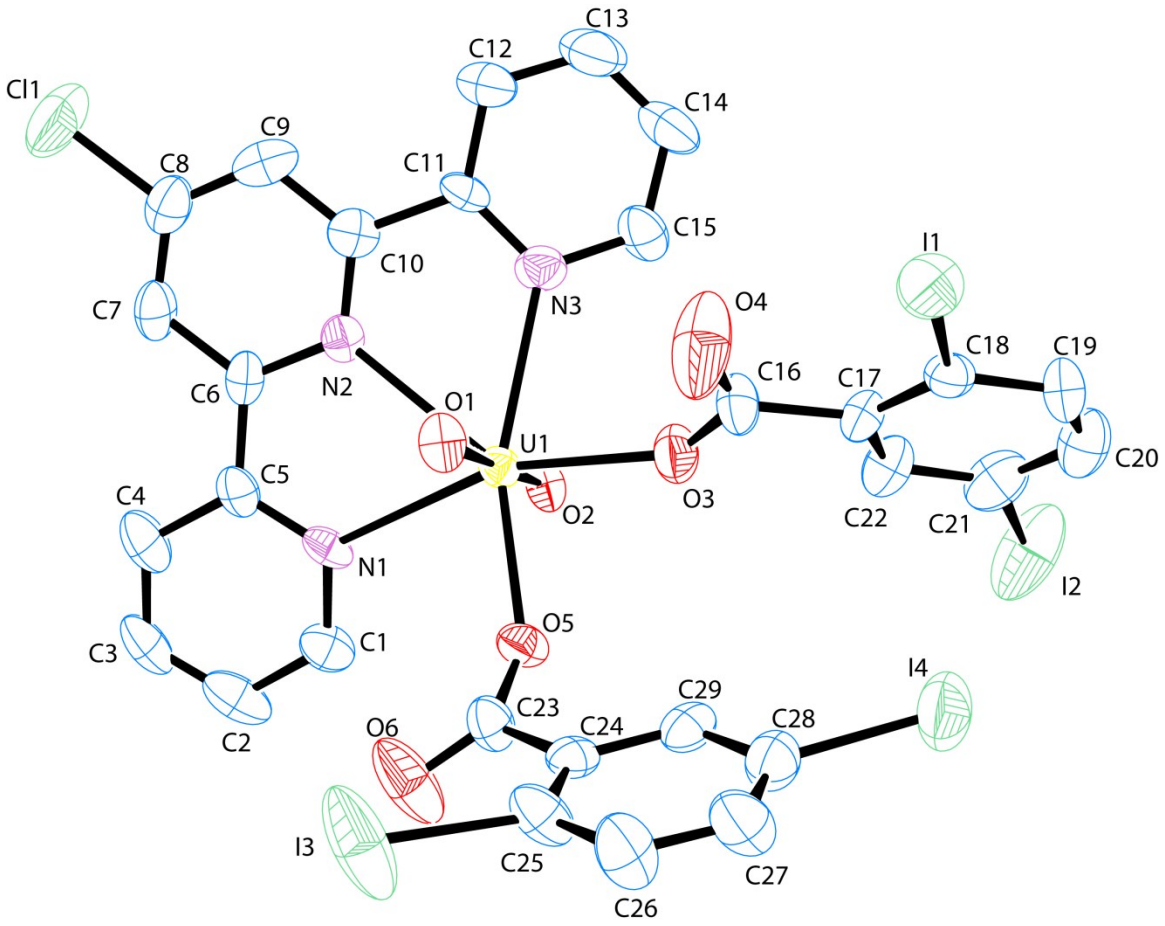

Figure S14 ORTEP illustration of complex **5**. Ellipsoids are shown at 50% probability level.

V. Tables of Bond Distances

Table S2 U-O Axial Bond Lengths in UO_2^{2+} complexes (**1-5)**

Complex	d_{U1-O1} [Å]	d_{U1-O2} [Å]	d_{U2-O7} [Å]	d_{U2-O8} [Å]
1	1.759(5)	1.766(6)		
2	1.756(5)	1.768(5)		
3	1.757(4)	1.749(4)	1.748(4)	1.758(4)
4	1.761(5)	1.760(5)		
5	1.752(7)	1.760(7)		

Table S3 U-O Equatorial Bond Lengths in UO_2^{2+} complexes (**1-5**)

Complex	d_{U1-O3} [Å]	d_{U1-O4} [Å]	d_{U1-O5} [Å]	d_{U1-O6} [Å]	d_{U2-O9} [Å]	d_{U2-O10} [Å]	d_{U2-O11} [Å]	d_{U2-O12} [Å]
1	2.463(5)	2.415(5)	2.458(5)	2.451(5)				
2	2.346(5)		2.286(5)					
3	2.480(4)	2.470(4)	2.505(4)	2.443(4)	2.492(4)	2.455(4)	2.484(4)	2.450(4)
4	2.275(5)		2.276(5)					
5	2.281(7)		2.270(7)					

Table S4 U-N Bond Lengths in UO_2^{2+} complexes (**1-5)**

Complex	d_{U1-N1} [Å]	d_{U1-N2} [Å]	d_{U1-N3} [Å]	d_{U2-N3} [Å]	d_{U2-N4} [Å]
1	2.638(6)	2.632(6)			
2	2.625(5)	2.587(6)			
3	2.657(5)	2.683(5)		2.668(5)	2.658(5)
4	2.555(6)	2.602(6)	2.585(6)		
5	2.583(8)	2.611(8)	2.561(9)		

VI. Bond Valence Summations

Table S5 Bond Valence Summations for hydroxide oxygen atom in Complex **2**

O5	Distance (Å)	Bond Valence Sum
Bound atoms		
U1	2.286	0.6285
U1’	2.341	0.5653
	Sum	1.194

Bond valence summations for selected oxygen atom in **2**. The values indicate that O5 is a hydroxyl group.[2, 3]

VII. References

1. K. P. Carter and C. L. Cahill, *Inorganic Chemistry Frontiers*, 2015, **2**, 141-156.
2. N. E. Brese and M. O'Keeffe, *Acta Crystallographica Section B*, 1991, **47**, 192-197.
3. P. C. Burns, R. C. Ewing and F. C. Hawthorne, *The Canadian Mineralogist*, 1997, **35**, 1551-1570.